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(54) A METHOD OF PRODUCING CELLULOSE PULP BY MEANS OF OXYGEN GAS DELIGNIFICATION

(71) We, MO OCH DOMSJO AB, a Swedish Body Corporate of Fack, S-891 01 Ornskoldsvik, Sweden, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of producing cellulose pulp. The method is intended to reduce the pollution hazards associated with conventional cellulose pulp manufacturing methods of the type envisaged and involves subjecting lignin containing cellulosic material, preferably wood, to an oxygen-gas digestion step, by which is meant a treatment step in which the wood is digested with oxygen gas in a solution, the pH of which is maintained within the range of 6.0—9.0 during the major part of the digestion process.

It is known that lignin containing material, such as wood, can be digested with alkaline reacting liquors in the presence of oxygen gas. It has been found extremely difficult, however, to obtain uniform digestion of the material, especially when the material is present in the form of coarse fragments. When treating wood in the form of chips, relatively rapid digestion is obtained with subsequent exposure of the cellulose fibres on the surface of the chips, while the interior of the chips remains undigested. If the digestion process is continued until the main portion of the core of the chips is also digested, the material on the surface of the chips becomes degraded to such a high extent that a pulp of very low viscosity is obtained. This pulp cannot be used for paper on which normal demands with respect to mechanical strength have been placed. Certain improvements in the properties of the pulp can be obtained by digesting the wood with oxygen gas-alkali at low-temperatures and high pressure, and by using a finely-divided lignin containing cellulosic material, but these improvements have not been of such magnitude as to warrant an

application of such processes on a technical scale.

Cellulose pulping is also known in processes for producing low yield pulps of low viscosity involving digesting cellulosic material with oxygen-gas and step-wise adding alkali to the system at pH 9.2—13.0 to treat the wood at elevated temperatures with an acid, neutral or alkaline aqueous solution in order to reduce the hemicellulose content of the pulp. It is not possible by this method, however, to obtain high yield pulps of high viscosity. Further, it is known from Canadian Patent No. 611,503 to digest wood with oxygen-gas and alkali at 120—160°C and a pH of 7.0—9.0. When the wood material is in the form of chips, this method presents the disadvantages of high alkali consumption and uneven digestion. In addition, the oxygen-gas becomes highly diluted with carbon dioxide, which increases the consumption of oxygen-gas.

It has now surprisingly been discovered that the aforementioned disadvantages can be substantially eliminated if the lignin-containing cellulosic material, preferably in the form of wood, is subjected to a pre-treatment step with a liquid to which is added a basic neutralizing agent, in a manner to dissolve a suitable quantity of the wood constituents, and then digest the material in the presence of oxygen gas under pressure in a liquid having a pH of between 6.0 and 9.0.

The present invention provides a method for producing cellulose pulp by digesting lignin-containing cellulose material such as wood, straw and bagasse, with oxygen in the presence of an aqueous solution containing a basic neutralizing agent, at a temperature of 100—180°C and a partial pressure of oxygen of 3—200 bars, wherein, prior to the digestion, the lignin containing cellulosic material is subjected to a pre-treatment step with a liquor containing a basic neutralization agent at a temperature of 60—200°C, suitably 100—170°C, and preferably 120—160°C, until

1—30% by weight, suitably 3—25% by weight and preferably 3—15% by weight based on the dry weight of the lignin containing cellulose material has passed into solution, the pH during the major portion of the oxygen digestion process being maintained at 6.0—9.0. It is particularly surprising that by carrying out the aforementioned combination of partly known procedural steps it is possible to obtain a high-yield pulp of high viscosity and good paper properties. Further, the method of the present invention enables for the first time a high yield pulp a high strength and degree of brightness to be produced without the use of sulphur as a digestion chemical.

In the pre-treatment step of the present invention a relationship prevails between temperature and treatment time, whereby, in order to obtain a specific desired degree of dissolution, a low temperature can be applied over a long period of time or conversely a high temperature over a short period of time.

The portion of the lignocellulosic material passing into solution is determined by removing the pre-treatment liquid by suction or by allowing the liquid to drain off, whereafter the material is washed with water to remove the remaining pre-treatment liquid. The residue is then dried and weighed. The quantity of material dissolved during the pre-treatment step is defined as the original dry weight minus the dry weight subsequent to the pre-treatment step and the washing step. When the pre-treatment step is effected under mild conditions, so that the amount of material dissolved lies within the range of 1—5% by weight, it is possible to determine accurately the quantity of material dissolved by establishing the quantity of acetic acid and non-volatile organic substances in the pre-treatment liquid.

The aforementioned and following pH values relate to measurements made with glass electrodes at room temperature on sample solutions taken from the pre-treatment step and the oxygen gas cooking step respectively during cooling. Further, it should be understood that the term basic neutralizing agent as used in accordance with the invention includes not only alkali metal hydroxides but also alkali metal carbonate and alkali metal bicarbonate and mixtures thereof. It has surprisingly been found suitable to use sodium carbonate as the basic agent during the pre-treatment step. According to the invention, the liquid used during the pre-treatment step contains the basic agent. During the pre-treatment step organic acids are formed, but it is not necessary for the liquid to present an alkaline reaction (i.e. pH higher than 7), and the pH may be allowed to fall to 6 without disadvantage. If it is desired to produce pulps having a low hemicellulose content, e.g. pulp intended for the manufacture of rayon,

the pre-treatment step of the present invention can be combined to advantage with an acid pre-hydrolysis, either as a separate first step or by allowing the pH in the pre-treatment liquid to fall temporarily to the desired level before adding the base used in the pre-treatment step of the present invention. Normally, the pH during the major part of the pre-treatment step is maintained at 7—14, suitably 7—9 and the pressure at 1—20 bars.

As previously mentioned, the method of the invention affords the unexpected effect whereby when using, for example wood chips a pulp of high viscosity is obtained, which pulp provides paper produced therefrom with superior strength qualities to pulps made by oxygen-gas digestion processes according to previously known methods. As with pulps produced by the direct oxygen-gas cooking of wood without subjecting the wood to the pre-treatment step of the present invention, an exceptionally high degree of brightness is obtained with the pulp produced in accordance with the invention as compared with pulps produced by known methods or alkali digestion processes, e.g. sulphate cooking and so-called soda cooking processes. By adapting the dissolution conditions in the pre-treatment step, the hemicellulose content of the pulp can be controlled to wide limits. Both pulps of exceptionally high yield (60—65% by weight in the case of birch) and pulps of approximately the same yield and hemicellulose content (e.g. 50—55% by weight yield with birch) as that obtained with conventional sulphate cooking processes, can be produced by the method of the present invention. In comparison with a direct oxygen-gas cooking process, it has been found that the method of the present invention, despite the fact that the base is used in two stages, affords a noticeably lower total consumption of base than in the case of a direct oxygen-gas cooking process when the pulp is digested to the same content of residual lignin. The difference in base consumption between the two methods has been found to reach approx. 5—10% by weight and to be mainly due to the amount of the wood material dissolved during the pre-treatment step. The greater the amount of material dissolved during the pre-treatment step, the greater the quantity of base saved. When the oxygen gas cooking process is effected with bicarbonate or carbonate, a further valuable advantage is obtained in the form of a reduction in the amount of carbon dioxide formed during the oxygen-gas cooking step.

Whereas the oxygen-gas cooking step takes place with oxygen gas under pressure, the pre-treatment step of the present invention is effected without increasing the pressure of the oxygen gas to above atmospheric. The pre-treatment step can be effected discontinuously

or continuously in conventional apparatus used for impregnating and cooking lignocellulosic material in chip form with different liquors, for example digestion and pre-hydrolysis. The presence of air does not affect the pre-treatment step in any way other than to render impregnation more difficult, and consequently, if desired, the air can be removed by known methods. The quantity of material, *inter alia* in the form of acetic acid and hemicellulose together with readily dissolved aromatic compounds and resin constituents, passing into solution during the pre-treatment step has an important significance on the quality and yield of the oxygen-gas digested pulp. If it is desired to produce a high yield oxygen-gas digested pulp having a high hemicellulose content, the amount of material dissolved in the first step should be in the order of 2—15% by weight on the dry weight of the original lignocellulosic material. The optimum quantity in this respect depends on the nature of the starting material and the use to which the final cellulose pulp is to be put. The temperature in the pre-treatment step should be 60—200°C. If the temperature is maintained below 100°C, it is desirable to have a comparatively long reaction time, e.g. from 6—12 hours. Temperatures higher than 170°C are normally uneconomical and it may be difficult to control the process at such temperatures. A particularly suitable temperature range is 100—170°C. In this way a reasonable reaction time of, e.g. 0.5—5 hours can be allowed without danger of the cellulose being decomposed. When producing paper pulp from wood chips, a temperature of 120 to 160°C and a treatment time of from 0.5—3 hours has been found particularly advantageous.

The liquor used to effect the pre-treatment step may contain or be prepared from a basic neutralizing agent, preferably an alkali metal hydroxide, alkali metal carbonate and/or alkali metal bicarbonate, sodium being preferred as the alkali metal for economic reasons. The pre-treatment liquor may also contain corresponding compounds of alkaline earth metals, e.g. calcium and magnesium. From a purely chemical aspect sodium hydroxide can be used to advantage when preparing the pre-treatment liquor and tests have shown that splendid results are obtained therewith. When wishing to produce pulps having a low hemicellulose content, it is particularly suitable to use sodium hydroxide. When wishing to produce high yield pulps, however, a still better result can be obtained by using sodium carbonate in preparing the pre-treatment liquor. In this respect there can be used to advantage sodium carbonate obtained by the wet combustion of waste liquor obtained from the pre-treatment step and/or the oxygen-gas cooking step, or by evaporating and subsequently burning said waste liquors. In this

way, there is obtained a closed system with which the chemicals can be recovered without difficulty. In accordance with another preferred embodiment, which is particularly suitable when washing to produce high-yield pulps of high hemicellulose content, the pre-treating liquor contains sodium bicarbonate. The liquor is suitably prepared by adding thereto sodium bicarbonate in solid form or in the form of an aqueous solution. Since the pH of the liquor is lower than that obtained when using hydroxide or carbonate, the hemicellulose in the pulp, primarily xylan and glucomanan, will depolymerize to only a slight degree, or possibly to no appreciable extent at all. All of the aforementioned advantageous technical effects are surprisingly obtained when subjecting the material to a very mild pre-treatment step with a bicarbonate solution, e.g. a charge of 10% by weight NaHCO_3 based on the dry weight of the lignin-containing cellulosic material and by heating the material to 120°C for one hour. The reason for this is still unclear, although it would seem to be due to a number of co-acting reactions and effects. One of these appears to be a de-acetylation of the wood, which in some way causes the reaction rate of the lignin relative to that of the carbohydrates to be higher during the subsequent oxygen-gas cooking stage than with an oxygen-gas cooking stage which is not preceded by a pre-treatment step. Further, apparently the accessibility of the lignin in the inner portions of the lignocellulosic material increases. It is particularly surprising that a clear effect is also obtained when the amount of material dissolved in the pre-treatment step only reaches to some few percent of the dry weight of the material.

During a pre-treatment step using liquors containing bicarbonate and/or carbonate, carbon dioxide is developed, which — if so desired — can be utilized in the known manner or be released to atmosphere without disadvantage. The removal of carbon dioxide from the system implies a marked advantage, particularly when using bicarbonate during the pre-treatment step, although the advantage is no less marked when using carbonate.

In accordance with a preferred embodiment for performing the actual oxygen-gas cooking step, the cooking step is also effected by adding to the system sodium carbonate and/or sodium bicarbonate or a mixture thereof, optionally replenished by adding sodium hydroxide.

This causes carbon dioxide to be formed during the oxygen-gas cooking step, which results in dilution of the oxygen gas. The carbon dioxide can be removed from the system by releasing the gaseous mixture from the digester, although this results in a high oxygen-gas consumption. Alternatively, the carbon dioxide can be removed by cooling the same. In accordance with a preferred embodi-

ment of the invention, carbon dioxide obtained during the oxygen-gas cooking step can be removed from the gas phase by absorption in an alkaline reacting liquor, e.g. a sodium carbonate solution. Sodium hydroxide may, to advantage, also be present in the absorption liquid. The sodium carbonate solution used may, to advantage, be a solution obtained by wet combustion or by combustion subsequent to evaporation of waste liquors obtained from the oxygen-gas cooking step and/or the pre-treatment step. The use of carbonate and above all, bicarbonate in the pre-treatment step according to the invention causes a significant quantity of carbon dioxide to be removed during the actual pre-treatment step, and the longer the pre-treatment step is continued the less carbon dioxide is formed during the actual oxygen-gas cooking step.

It has been found particularly suitable to maintain the carbon dioxide pressure during the major portion of the oxygen cooking step at 0.2—5 bars. An excessively high carbon dioxide pressure results in a lowering of the cooking rate, although this can be counteracted within certain limits by increasing the temperature. A reduction in the carbon dioxide pressure leads to an increase in the pH of the cooking liquor, which results in increased decomposition of the carbohydrates. The limits recited here relate to the manufacture of paper pulp when using sodium carbonate and sodium bicarbonate as the active alkali ingredient. In such cases the carbon dioxide is enriched in the system. If the system is closed and sodium is recovered in the form of sodium carbonate in the aforementioned manner, the carbon dioxide must be removed in some way or another. A particularly advantageous method in this respect is to use sodium carbonate as an absorption liquid for carbon dioxide in the oxygen-gas and to utilize used absorption liquid in the pre-treatment step. In spite of these measures a certain excess of carbon dioxide may be obtained, and this excess can be removed in the previously indicated manner or by other known methods, such as causticizing the carbonate solution or heating bicarbonate in solid form or in solution to such temperatures that carbon dioxide is expelled, or may be blown off by venting and/or by injecting air, for example, into the system.

Thus, the introduction of a pre-treatment step with sodium carbonate, preferably a pre-treatment step with sodium bicarbonate, with which carbon dioxide formed in the system is expelled therefrom, considerably relieves the system of carbon dioxide.

In this connection it should be mentioned that, in addition to carbon dioxide, carbon monoxide is also formed during the oxygen-gas cooking process, which should be taken into account in view of the explosion and poison

risks incurred thereby. This problem is solved by maintaining the carbon monoxide content in the oxygen-gas digester at a level below the explosion limit. This is suitably effected by removing a portion of the carbon monoxide from the system, by releasing the gases from the cooker in a safe manner, optionally after having first purified the gases by known methods. Alternatively, the gases may be used in connection with wet combustion processes or other form of combustion processes, so that the carbon monoxide is rendered safe by oxidation. When the active alkali ingredient used in the cooking process is bicarbonate or carbonate, carbon dioxide will, of course, also be removed when removing carbon monoxide.

In the case of plants applying the method of the present invention together with other cellulose manufacturing processes, e.g. sodium sulphite — sodium bisulphite — sulphate — and polysulphide cooking processes, the chemical recovery systems may, to advantage, be coordinated, e.g. through common combustion systems. In such cases, the pre-treatment steps of the present invention may be effected to advantage with a sulphide containing solution e.g. green liquor, wherewith the pre-treatment step may serve as a means for expelling hydrogen sulphide.

With respect to the aspect of heat economy and chemical recovery, the pre-treatment liquor used in accordance with the invention should preferably contain organic substances returned from the pre-treatment step i.e. from a previous cellulosic material treatment process and separated therefrom, before the material is passed to the oxygen gas cooking process. The liquor can therewith be replenished with chemicals, e.g. hydroxide, carbonate and/or bicarbonate, before it is reused.

According to a preferred embodiment of the invention, waste liquor obtained from the oxygen-gas cooking process is used to prepare the liquor used for the pre-treatment step. Preferably waste liquor from the oxygen-gas cooking step recovered when washing the ready cooked pulp and diluted with water or with an aqueous solution, e.g. bleaching liquor or evaporation condensate is used. It is also suitable in this embodiment to return liquor from the pre-treatment step.

Subsequent to terminating a pre-treatment step it has been found particularly suitable to wash pre-treatment liquor from the cellulosic material with waste liquor obtained from the oxygen-gas cooking process and/or with solutions containing bleaching liquor. The resulting liquid mixture is returned to advantage to the pre-treatment step and used in a subsequent pre-treatment process, optionally subsequent to replenishing the liquid with alkali. This washing step has been found to

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afford advantages with respect to the homogeneity of the oxygen-gas cooking process, although it is not an essential feature of the method according to the invention. In many instances it is sufficient to allow the used pre-treatment liquor to drain from the cellulose material before the material is passed to the oxygen-gas cooking step.

It has also been found advantageous to press the pre-treated cellulosic material mechanically subsequent to the pre-treatment step, e.g. by passing the material through one or more roller presses. The material can be pressed to advantage subsequent to removing pre-treatment liquor totally or partially therefrom by washing the material with waste liquor obtained from the oxygen gas cooking step, by which is meant here liquid containing such waste liquor. Pressing of the lignocellulosic material increases the accessibility of the internal portions of the material to the chemicals, thereby affording improved strength properties and higher viscosity of the finished material.

The accessibility of the internal portions of the material to the chemicals can also be improved by introducing a different type of mild mechanical treatment, e.g. in a peg shredder, behind the pre-treatment step, so that the cellulose material is disintegrated along fractured impressions in the material. The mechanical pressing operation or the alternative mild mechanical treatment process may also be carried out subsequent to adding the chemicals intended for the cooking step.

The pre-treatment process may be carried out continuously or discontinuously, and the basic agent used in the pre-treatment step may be added continuously, discontinuously or in one single batch. When wishing to manufacture a pulp of low hemicellulose content, and therefore desiring to use sodium hydroxide as the basic agent in the pre-treatment process, it is suitable with respect to the balance of carbon dioxide in the system, if the oxygen-gas cooking process is effected with sodium carbonate and/or bicarbonate, to treat the material in the pre-treatment step first with bicarbonate and then with carbonate and finally with sodium hydroxide. Formed carbon dioxide should be removed from the system before the sodium hydroxide is added thereto. For pulps having a high hemicellulose content it may be suitable to treat the material first with sodium bicarbonate and then with sodium carbonate, and to exclude the sodium hydroxide treatment step.

The quality of the pulp produced in accordance with the invention is determined to a greater extent by dissolution of the material during the pre-treatment step than by the quantity of active alkali charged to the pre-treatment liquor. The pre-treatment waste liquor can be returned to the pre-treatment

step, and indeed should be under normal conditions in order to obtain good heat economy. In connection therewith, active basic agent may also be returned. The return of the pre-treatment waste liquor and active basic agent affords marked advantages with respect to the speed of the pre-treatment reactions. The quantity of active basic material present in the pre-treatment step may therefore be greater than the quantity consumed and is generally not critical, provided that a moderate temperature is applied. The amount of active basic material consumed during the pre-treatment step in the form of sodium bicarbonate or calculated as sodium bicarbonate (on an equimolar basis with respect to sodium) normally reaches to 3—35% by weight, suitably 5—20% by weight, preferably 8—15% by weight based on the dry weight of the lignocellulosic material. The quantity 8—15% by weight has been found particularly suitable for most types of paper pulp. With respect to high-yield pulps, however, this quantity may be lower, and may be higher in the case of pulps of low hemicellulose content.

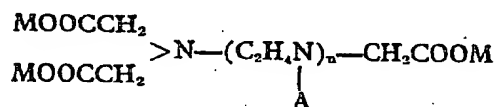
The quantities of active base mentioned above relate to the quantity of base consumed in the pre-treatment step, at steady state. The quantity of active base present during the pre-treatment step can be higher without damaging the pulp. In those instances when it is desired to pass the pulp directly to the oxygen-gas cooking step without washing the pulp after the pre-treatment step, some or all of the base needed for the oxygen-gas cooking step can be charged to the system during the pre-treatment step or to the original treatment liquor. In such a case, the expedient of pressing the cellulosic material prior to the oxygen-gas cooking step affords a marked advantage.

When producing cellulose pulps for specific usages, e.g. for producing paper having a high resistance to color reversion (long shelf life) it is suitable to add to the liquor used for the pre-treatment step a surface tension reducing agent. Nonionic, anionic and cationic agents may be used in this respect. Such agents may also be present to advantage during the actual oxygen-gas cooking step. Foam preventing agents can also be charged to advantage to the oxygen-gas cooking step.

With respect to the brightness of the pulp produced, it has been found suitable in certain circumstances to introduce an oxidation agent, e.g. a peroxide, to the pre-treatment liquor.

The addition of reducing agents, e.g. dithionite and/or hydrioborate (borohydride) to the pre-treatment liquor has also been found advantageous with respect to the strength and brightness of the pulp. This addition, similarly to the previously mentioned additions, can be made either to the original pre-treatment liquor or to the system during the pre-treatment step.

With certain types of lignocellulosic material, especially such containing large quantity of transition metals, such as copper, cobalt and iron, it is suitable that the pre-treatment liquor contains complexing agents producing soluble compounds with metals. In this way decomposition of the cellulose can be reduced during the subsequent oxygen-gas cooking step. Examples of suitable complexing agents are polyphosphates and aminopoly carboxylic acids, e.g. such having the general formula



where A is the group $-\text{CH}_2\text{COOM}$ or $-\text{CH}_2\text{CH}_2\text{OH}$, M is hydrogen or an alkali metal and n is an integer between 0 and 5. Further examples of suitable complexing agents are ethylenediamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and diethylenetriamine pentaacetic acid (DTPA). Hydroxy carboxylic acids of the type aldonic acids, e.g. gluconic acid and saccharic acids and aldaric acids, and similarly organic amines, e.g. ethylenediamine can be used. Alternatively, these complexing agents can be added subsequent to completing the pre-treatment step. It is often suitable to add the complexing agents to the cellulosic material before the material is brought into contact with the pre-treatment liquor. When producing high-yield cellulose pulps, the oxygen-gas cooking step is suitably carried out with a cooking liquor containing substantially sodium bicarbonate as the active base. The sodium bicarbonate is suitably prepared from sodium carbonate obtained by the combustion of waste liquor and subsequent absorption of carbon dioxide from the oxygen-gas used during the cooking operation, by means of an aqueous solution containing sodium carbonate. The aqueous solution may, to advantage, contain waste liquor obtained either from the pre-treatment step or from the oxygen-gas cooking step or from both.

A reduced load with respect to the removal of carbon dioxide from the oxygen-gas cooking step is obtained by effecting the cook with a cooking liquor containing mainly sodium bicarbonate and sodium carbonate as the active base. This liquor can of course be obtained by adding the two chemicals in solution or in solid form. Another method, effectively contributing to expelling carbon dioxide from the system, is to prepare the cooking liquor from bicarbonate and before it is introduced or returned to the cooking step expel a suitable quantity of the carbon dioxide at elevated temperature so that a mixture of sodium bicarbonate and sodium carbonate is obtained.

The method of the present invention is particularly suited for producing high-yield cellulose pulps with a high degree of brightness. To obtain the least possible decomposition of the cellulose molecules and good paper properties it is suitable to charge the active base stepwise or continuously during the oxygen-gas cooking step, to replace consumed active alkali and to maintain the pH of the cooking liquor at the desired level. It is particularly suitable to maintain the pH within the range of 6.5—8.5 during the major part of the process. Very good results were obtained with experiments in which the pH was held at 7—7.2 for approximately 70% of the time and at 6.2—7 for approximately 30% of the cooking time. Base was charged to the system in the form of bicarbonate at time intervals of 15 mins. and the charge based on the measured pH with the intention of maintaining a value of approximately 7.

When using birch chips as the starting material, a still higher yield and still lower decomposition of the cellulose is obtained if during the oxygen-gas step the pH is maintained within the range of 7—7.5. It is suitable to measure the pH continuously and to meter the alkali to the system automatically so that the desired pH can be obtained.

It is also suitable that an inhibitor against the decomposition of carbohydrates is present in the system during the oxygen-gas cooking step and/or a subsequent oxygen-gas bleaching step if used. The inhibitors used in this respect are magnesium compounds, e.g. magnesium sulphate, magnesium carbonate and/or complex magnesium compounds. If the cooking step is carried out at a high pH, e.g. pH 9, the use of magnesium compounds is particularly important.

In addition to the selection of different types of basic agent (bicarbonate, carbonate and hydroxide) and in addition to making such charges successively as the base is consumed, the pH may be regulated by controlling the partial pressure of the carbon dioxide during the oxygen-gas cooking step. If high temperatures and high partial pressures with respect to oxygen-gas were applied, a high carbon dioxide pressure, e.g. of 5 bars, can be used. If the cooking step is performed with a low oxygen-gas pressure, a lower carbon dioxide pressure should be maintained, suitably 0.2—1 bar.

The oxygen-gas cooking step can be effected under conditions whereby the cellulosic material is completely immersed in the cooking liquor, which must naturally be kept circulating so that newly dissolved oxygen-gas is supplied through the cooking liquor. Frequently more advantageous results have been obtained when the cooking step has been performed with the cellulosic material (e.g. the chips) in contact with both the circulating cooking liquor, which

is sprayed over the material, and the oxygen-gas under pressure. Similar cooking processes in which cellulosic material is treated with cooking liquor without being immersed therein are known and applied in the art and the type of apparatus for the actual oxygen-gas cooking step may thus be of known construction. As is well known, when applying any of these two methods it is important that the oxygen-gas is in intimate contact with the cooking liquor so that good mass transfer is obtained. Apparatus constructed for this purpose are known to the art. With respect to the necessary cooking time and the necessary oxygen-gas pressure, the cooking step is effected more favourably if the concentration of oxygen in the cooking liquor is as close to saturation point as possible.

It has also been found possible to perform the oxygen-gas cooking step in the form of a pure gas phase cooking step, i.e. a reaction without liquid circulation. This is effected by impregnating the material with cooking liquor, whereafter the material is allowed to drain to remove surplus liquor therefrom. Squeezing of the material, i.e. the chips, to a dry content of, for example, 27—34% or higher, e.g. 45%, has been found to afford a very uniform reaction. In this instance, the oxygen-gas cooking step can be effected in apparatus of the type known for the oxygen-gas bleaching of cellulose pulp. Alternatively, the cooking chemicals may comprise active alkali remaining from the pre-treatment step. Owing to the low degree of solubility of sodium carbonate and sodium bicarbonate, a single stage gas phase cooking step can only be applied in this way if the charge during the actual cooking step is low. The method can be combined with any of the two previously mentioned methods or, subsequent to a first gas phase cooking step, the cellulosic material may be impregnated with fresh cooking liquor, which is then removed e.g. by draining and pressing, whereafter the material is subjected to a cooking process in a new gas phase step.

When applying the most important cellulosic raw material wood, it is advantageous to use it in finely-divided form, e.g. in the form of saw-dust or wood shavings. The most common form of lignocellulosic material in conventional wood digestion processes is, however, wood chips. Chips of conventional type can be used when applying the method of the present invention. It has been found, however, that chips of small thickness are to be preferred to relatively thick chips. Tests have shown that a particularly advantageous result, such as short cook time in the oxygen gas cooking step, low chives content and high pulp viscosity is obtained if chips are used which have been split in the direction of the fibres in the chipper. Splitting of the chips need not be done so effectively that chip fragments

are divided into smaller pieces. Very good results have been obtained with coarse chips containing a large number of cracks in the fibre direction. Apparently these cracks facilitate penetration of the chemicals into the chip fragments.

Instead of splitting the chips as the chips are cut, the chips may be split in a subsequent step. Cracks which extend in the longitudinal direction of the fibres can be produced by pressing the chips in a roller press for example, or by treating the chips in a shredder.

As a result of its high degree of brightness, the pulp produced in accordance with the method of the present invention can be used directly for many purposes without being subjected to a bleaching step, e.g. in the manufacture of paper and cardboard. The pulps may also be bleached to a very high degree of brightness by means of conventional bleaching agents in one or preferably more steps.

The invention will now be illustrated with reference to a number of examples taken from systematically performed experiments using birch chips as a starting material. The invention, however, is not restricted to birch chips, but can be generally applied to different types of lignocellulosic material. When using wood in chip form, hardwood has been found more easily digested than softwood. Under comparable conditions a somewhat larger content of screening rejects and a lower degree of brightness is obtained with softwood. The rejects however, can be subjected to renewed oxygen-gas digestion and the method can therefore also be applied to softwood when in chip form.

The following Examples are given to illustrate the invention.

EXAMPLE 1.

4 mm thick birch chips were pre-treated in an autoclave with solutions of NaHCO_3 , Na_2CO_3 and NaOH . The pre-treatment step was carried out for one hour at a temperature of 120°C and the pre-treatment liquor contained 8.2 g of organic substance per liter, from a previous pre-treatment step. With the tests in which bicarbonate and carbonate were used CO_2 gas developed during the pre-treatment was discharged to atmosphere. The chip fragments were drained of the treatment liquor and then washed for five minutes with waste liquor obtained from the oxygen-gas step. The quantity of organic substance dissolved (determined subsequent to washing a chip sample thoroughly with water) was found to correspond to 3% by weight on the dry weight of the wood. The chips were then subjected to digestion with oxygen-gas in the presence of bicarbonate, the bicarbonate charge corresponding to 39% by weight based on the

dry weight of the original chips. The pH of the treating liquor was 8.5 at the start of the digestion and 7.7 at conclusion of digestion. The oxygen-gas digestion step was continued for 6 hours at 140°C and a partial pressure of oxygen-gas of 7 bars. The carbon dioxide pressure was maintained within the interval 0.1—0.2 bar by treating the circulating oxygen-gas with sodium carbonate solution.

The wood liquor ratio was 1:7 during the pre-treatment step and 1:14 during the oxygen-gas cooking step, this latter step being carried out in a circulation cooker in which the cooking liquor was sprayed over the chips. By way of comparison, two reference tests were carried out without the pre-treatment step and with a bicarbonate charge of 49 and 39% by weight respectively.

| Pre-treatment | NaHCO ₃ during oxygen-gas digestion step % | Total yield % | Screened yield % | Kappa No. | Viscosity cm ³ /g | Brightness % |
|--------------------------------------|---|---------------|------------------|-----------|------------------------------|--------------|
| None | 49 | 55.1 | 53.1 | 12.1 | 633 | 63.1 |
| None | 39 | 60.5 | 51.9 | 17.1 | 719 | 59.0 |
| NaHCO ₃ , 10% | 39 | 58.4 | 56.4 | 13.3 | 746 | 65.9 |
| Na ₂ CO ₃ , 5% | 39 | 61.2 | 59.2 | 14.7 | 754 | 66.1 |
| NaOH, 4.8% | 39 | 59.1 | 55.9 | 15.6 | 701 | 66.4 |

The charge of chemicals to the system and the yield are calculated here and in the following in percent by weight based on the dry weight of the wood charged. The analyses given above and hereinafter were made according to Scandinavian Standards (SCAN).

The test — with which all the active alkali was present at the beginning of the oxygen-gas cooking step — showed that pre-treatment steps using respectively sodium bicarbonate, sodium carbonate and sodium hydroxide result in an increase in yield of screened pulp. The highest values with respect to viscosity were obtained with the pre-treatment steps using sodium bicarbonate and sodium carbonate. The pre-treatment steps also resulted in an increase in the brightness of the finally cooked pulp.

EXAMPLE 2.

Birch chips from the same batch as those treated in Example 1 were pre-treated with NaHCO₃ and NaOH respectively in the aforementioned manner. At the beginning of the

oxygen-gas digestion step 5% by weight of sodium bicarbonate based on the dry weight of the wood was charged to the system. During the digestion step the pH was maintained between 6.5 and 7.5, by continuously adding bicarbonate. The conditions in other respects were the same as those in the tests of Example 1. In the tests of Example 2 a much higher shive content was obtained with the same cooking times as those applied in the tests of Example 1, but when the cooking time was extended to 8 hours high-yield pulps having a high viscosity were obtained. The results are shown in the following table. A reference test carried out without the inclusion of a pre-treatment step but with the same total charge of NaHCO₃ as that used in the test embodying a pre-treatment step with NaHCO₃ resulted in a shive content of roughly 40% by weight. In order to reduce the shive content to 10% by weight, it is necessary to increase the total charge of NaHCO₃ from 28 to 37% by weight.

| Pre-treatment | NaHCO ₃ during oxygen-gas digestion step % | Total yield % | Screened yield % | Kappa No. | Viscosity cm ³ /g | Brightness % |
|--------------------------|---|---------------|------------------|-----------|------------------------------|--------------|
| NaOH, 4.8% | 5+13 | 59.8 | 52.8 | 19.9 | 881 | 59.7 |
| NaHCO ₃ , 10% | 5+13 | 63.9 | 59.5 | 21.1 | 927 | 58.7 |
| None | 5+32 | 62.7 | 52.7 | 19.9 | 810 | 57.2 |

As shown by the table, the combination of a pre-treatment step and successive addition of active alkali (NaHCO_3) during the digestion process affords marked advantages. If the pre-treatment step is excluded, the shive content increases strongly with the same total alkali charge. This increase in shive content can be counteracted by increasing the quantity of NaHCO_3 charged during the digestion process, but this results in a marked decrease in viscosity, i.e. a more severe degradation of the cellulose molecules. The tests also show that bicarbonate is more suitable than hydroxide.

Tests in which the cooking liquor was prepared from cooking liquor returned from a preceding experiment replenished with NaHCO_3 showed that, under otherwise constant conditions, the viscosity levels compared at constant kappa number of the finished pulp were roughly 10% lower. Upon raising the partial pressure of the oxygen-gas to 14 bars, pulps were obtained with the same viscosity of those obtained when cooking with pure bicarbonate solution at an oxygen partial pressure of 7 bars.

EXAMPLE 3.

Two different types of birch chips, having a thickness of 2 and 5 mm respectively were pretreated in an autoclave with a sodium bicarbonate solution for two hours, formed carbon dioxide being released after heating period of 30, 60 and 90 minutes. The chips were then drained of pretreatment liquor and passed through a roller press.

The pressed chips were then subjected to an oxygen-gas digestion step in the presence of sodium bicarbonate for 8 hours at 140°C . At the beginning of the digestion step 5% by weight NaHCO_3 was charged to the system, whose pH was then 7.8, whereafter 11% by weight calculated on the dry weight of the wood was added continuously during the digestion process to maintain the pH between 7.5 and 8.0. The partial pressure of oxygen gas was 7 bars and the partial pressure of carbon dioxide 0.2—0.3 bar. The conditions in other respects were the same as those in Example 1. The results are given in the table below.

| Pre-treatment | NaHCO_3 during oxygen-gas digestion % | Dissolution during pre-treatment step % | Total yield % | Screened yield % | Kappa number | Visc. cm^3/g | Brightness % |
|--|--|---|---------------|------------------|--------------|------------------------------|--------------|
| 30% NaHCO_3 , 130°C | 5+11 | 5 | 65.4 | 54.9 | 18.6 | 939 | 60.7 |
| 20% NaHCO_3 , 160°C | 5+11 | 11 | 60.5 | 53.5 | 11.1 | 942 | 62.2 |
| None | 36 | | 66.6 | 42.2 | 22.1 | 817 | 54.9 |
| 30% NaHCO_3 , 130°C | 5+11 | 5 | 57.9 | 53.4 | 16.7 | 903 | 58.7 |
| 20% NaHCO_3 , 140°C | 5+11 | 8 | 56.0 | 55.0 | 11.1 | 859 | 57.8 |
| 20% NaHCO_3 , 160°C | 5+11 | 12 | 54.2 | 52.2 | 10.8 | 913 | 59.1 |
| None | 36 | | 62.7 | 52.7 | 19.9 | 810 | 57.2 |

As will be seen from the table, a pre-treatment step with a sodium bicarbonate solution at 130—160°C results in a marked decrease in the shive content, reduced kappa number and increase in viscosity of the screened pulp. The reject obtained from the screening process can be subjected to a new oxygen-gas digestion process, the shives providing a pulp with low kappa number and a high degree of brightness. As with the tests made in the other Examples, it was found that re-cook with NaHCO₃ produced a pulp of higher viscosity than that obtained with oxygen-gas digestion processes in which NaOH was used as the active alkali ingredient.

WHAT WE CLAIM IS:—

1. A method of producing cellulose pulp by (a) treating lignocellulosic material with a liquor containing a basic neutralising agent at 60—200°C until 1—30% by weight based on the dry weight of the lignocellulosic material has passed into solution and then (b) digesting the lignocellulosic material with oxygen in the presence of an aqueous solution containing a basic neutralising agent at a temperature of 100—180°C and an oxygen partial pressure of 3—200 bars, the pH being maintained at 6—9 during the major part of the oxygen digestion.
2. A method according to claim 1 wherein the temperature in step (a) is 100—170°C.
3. A method according to claim 2 wherein the temperature is 120—160°C.
4. A method according to any one of the preceding claims wherein step (a) is continued until 3—25% by weight of the material dissolves.
5. A method according to claim 4 wherein step (a) is continued until 3—15% by weight of the material dissolves.
6. A method according to any one of the preceding claims wherein the pH is maintained at 7—14, and the pressure at 1—20 bars during the major part of step (a).
7. A method according to claim 6 wherein the pH is 7—9.
8. A method according to any one of the preceding claims wherein a liquor is used for step (a) which contains sodium carbonate or which is prepared by adding sodium carbonate thereto.
9. A method according to any one of claims 1—7, wherein a liquor is used for step (a) which contains sodium bicarbonate or which is prepared by adding sodium bicarbonate thereto.
10. A method according to any one of the preceding claims wherein the liquor used for step (a) contains or is prepared from waste liquor obtained from the oxygen-gas digestion process.
11. A method according to any one of the preceding claims wherein the step (a) liquor

is washed either completely or partially from the cellulosic material upon completion of step (a) with waste liquor obtained from the oxygen-gas digestion process.

12. A method according to any one of the preceding claims wherein the cellulosic material obtained from step (a) is subjected to a mechanical working operation upon completion of step (a).

13. A method according to claim 12 wherein the working operation involves pressing the material through at least one roll nip press.

14. A method according to any one of the preceding claims, wherein the quantity of basic neutralising agent consumed during step (a) in the form of sodium bicarbonate or calculated as sodium bicarbonate is 3—35% by weight of the dry weight of the lignocellulosic material.

15. A method according to claim 14 wherein the quantity is 5—20% by weight.

16. A method according to claim 15 wherein the quantity is 8—15% by weight.

17. A method according to any one of the preceding claims, wherein a surface tension reducing agent is mixed with the step (a) liquor.

18. A method according to any one of the preceding claims, wherein an oxidation agent is mixed with the step (a) liquor.

19. A method according to claim 18 wherein the oxidation agent is a peroxide.

20. A method according to any one of claims 1—17 wherein a reducing agent is mixed with the step (a) liquor.

21. A method according to claim 20 wherein the reducing agent is a dithionate and/or a borohydride.

22. A method according to any one of the preceding claims wherein a complexing agent for the transition metals is mixed with the step (a) liquor.

23. A method according to claim 22 wherein the complexing agent is a polyphosphate, nitrogenous polycarboxylic acid and/or hydroxy carboxylic acid.

24. A method according to any one of the preceding claims wherein the pH of the digesting solution is held at 6.5—8.5 during the major part of the digestion process.

25. A method according to any one of the preceding claims, wherein the digestion process is carried out with a solution containing mainly sodium bicarbonate as the basic neutralising agent.

26. A method according to any one of claims 1—24, wherein the digestion process is carried out with a solution containing mainly sodium bicarbonate and sodium carbonate as the basic neutralising agent.

27. A method according to any one of the preceding claims, wherein active alkali in the form of sodium hydroxide, sodium carbonate and/or sodium bicarbonate is added stepwise

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- or continuously during the oxygen gas digestion process to replace consumed active alkali and to maintain the solution at the desired pH.
- 5 28. A method according to any one of the preceding claims, wherein carbon dioxide is removed from the gas phase during the oxygen gas digestion phase.
- 10 29. A method according to claim 28 wherein carbon dioxide is removed by absorption in an alkaline reacting liquid, such as a sodium carbonate solution.
- 15 30. A method according to any one of the preceding claims, wherein the partial pressure of the carbon dioxide is maintained at 0.2—5 bars during the major part of the oxygen-gas digestion process.
31. A method according to any one of the preceding claims, wherein the oxygen-gas digestion is effected in a plurality of steps, of which at least one is a gas phase digestion step. 20
32. A method according to claim 1, substantially as hereinbefore described.
33. Cellulose pulp obtained by a method according to any one of the preceding claims. 25

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